

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
23 May 2002 (23.05.2002)

PCT

(10) International Publication Number
WO 02/39962 A1

(51) International Patent Classification⁷: **A61K 7/025**

(21) International Application Number: PCT/US01/43485

(22) International Filing Date:
16 November 2001 (16.11.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/714,715 16 November 2000 (16.11.2000) US

(71) Applicant (for all designated States except US): **AVON PRODUCTS, INC.** [US/US]; 1251 Avenue of the Americas, New York, NY 10020-1196 (US).

(71) Applicants and

(72) Inventors: **FARER, Alan** [US/US]; 91 Alize Drive, Kinnelon, NJ 07405 (US). **LEE, Christian, J.** [US/US]; 48 Winding Way, Parsippany, NJ 07054 (US).

(74) Agent: **RUGGIERO, Charles, N., J.**; Ohlandt, Greeley, Ruggiero & Perle, L.L.P., 10th floor, One Landmark Square, Stamford, CT 06901-2682 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/39962 A1

(54) Title: COSMETIC COMPOSITIONS CONTAINING POLYURETHANE

(57) Abstract: There is provided a cosmetic composition, preferably in the form of a nail polish, comprising a primary film former, one or more high-molecular weight polyurethanes, and, optionally, one or more arylsulfonamide epoxy resins.

COSMETIC COMPOSITIONS CONTAINING POLYURETHANE

BACKGROUND OF THE INVENTION

5 1. Field of the Invention

The present invention relates generally to cosmetic compositions. More particularly, the present invention relates to cosmetic compositions with film-forming agents for application to the skin and nails.

10 2. Description of the Prior Art

Desirable cosmetic characteristics of film-forming cosmetic compositions include: good application, the production of a uniform film of excellent sheen or gloss, rapid drying time, good adhesion, a certain amount of flexibility, and good film strength to avoid cracking and flaking of
15 the film. Moreover, an often overlooked, but desired, characteristic is the absence of irritation of the skin, hair, and/or nails upon which the film-forming cosmetic composition is applied.

To achieve the above-identified characteristics, film-forming cosmetic compositions conventionally have a mixture of film forming
20 agents. Typically, cellulose-based film formers, in particular, nitrocellulose or cellulose acetate butyrate, are used as "primary" film formers. Often, the primary film formers are combined with one or more "secondary" film formers, which increase the film-forming ability of the primary film former

and improve the sheen and adhesion of the resulting films. Secondary film formers known in the art include alkyd resins, polyester resins, acrylic resins, low molecular weight polyurethane resins, polyamide resins, vinyl resins, arylsulfonamide aldehyde resins, and arylsulfonamide epoxy resins.

5 For example, U.S. Patent No. 5,676,935 to Mellul et al. discloses that nitrocellulose, arylsulphonamide-epoxy resin, and polyurethane have been used as film-forming materials. However, polyurethanes presently used in the art are difficult to stabilize in pigmented cosmetic compositions. Generally, combining polyurethane resins and pigments within a single
10 cosmetic composition results in the pigments falling out of the suspension, which is clearly undesirable.

U.S. Patent No. 6,080,413 to Ellingson et al. is directed to polyurethane nail polish compositions that have from about 0.1% to about 40% by weight of a water-insoluble, film-forming polyurethane, and a
15 carrier having a liquid diluent. The diluent has water, and one or more volatile organic solvents.

U.S. Patent No. 6,123,931 also to Ellingson et al. is directed to polyurethane and polyacryl nail polish compositions. These compositions have from about 0.1% to about 40% by weight of a water-insoluble, film-
20 forming polymer, water, and one or more volatile organic solvents. However, the polymer is one or more polyacryls, polymethacryls, polyurethane-polyacryl mixtures, polyurethane-polymethacryl mixtures, urethane-acryl copolymers, and mixtures thereof.

Notwithstanding the foregoing, it has been unexpectedly discovered that a cosmetic composition, particularly a nail enamel composition, including a cellulose-based primary film forming agent, in combination with one or more high molecular weight polyurethane resins as a secondary film forming and plasticizing agent, and, optionally, one or more epoxy resins, results in increased adhesion of the cosmetic composition onto the nail, superior flexibility (displacement), durability, film strength, and no significant loss of gloss over time.

Moreover, unlike conventional nail enamel compositions where the pigmented nail enamel coating transfers coating if the nails are rubbed onto, for example, a paper napkin, notwithstanding that the initial drying time (10 to 60 minutes) has passed and the nails appear perceptively dry, the nail enamel coating of the present composition is significantly more transfer resistant once the nails are perceptively dry.

15

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a cosmetic composition with a combination of film-forming agents for application to the skin and nails.

It is another objective of the present invention to provide such a cosmetic composition having improved gloss, wear-resistance, adhesion, and flexibility and is more transfer resistant in less time.

These and other objects of the present invention are achieved by a cosmetic composition, preferably in the form of a nail polish, comprising a cellulose-based primary film former, one or more high molecular weight polyurethanes, and, optionally, one or more arylsulfonamide epoxy resins.

5

DETAILED DESCRIPTION OF THE INVENTION

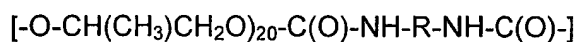
The present invention provides a cosmetic composition, preferably in the form of a nail polish or other film-forming cosmetic composition. The composition has at least one primary film forming material and one or more
10 high molecular weight polyurethane resins. Optionally, the cosmetic composition has at least one arylsulfonamide epoxy resin.

Preferably, the primary film former is a cellulose-based film former. More preferably, nitrocellulose is the primary film former. However, many cellulose-based materials, such as cellulose acetate, cellulose acetate
15 butyrate, and ethyl cellulose, may be used either in combination with or as an alternative to nitrocellulose.

The cellulose-based primary film former is preferably present in an amount about 5 percent by weight (wt%) of the total weight of the composition to about 15 wt%. More preferably, the primary film former is
20 about 7 wt% to about 12.5 wt% of the total weight of the composition.

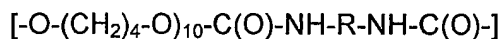
An essential aspect of the present invention is the use of one or more high molecular weight polyurethane resins, which function as both film formers and plasticizers. Preferably the high molecular-weight

polyurethane resins are polyether-type, high-molecular weight, polyurethane resins having an average molecular weight (MW) in the range of about 20,000 to about 80,000. The t_g (glass transition temperature) of the preferred high-MW polyurethane resins is in the range of about -4°C to about -20°C and, more preferably, about -19°C. More preferred high-MW polyurethane resins have one of the following structures:



Structure 1

10



Structure 2

wherein R is an aliphatic moiety. Aliphatic polyurethane resins are preferred because they are more stable than aromatic polyurethane resins.

The high-MW polyurethane resins on a percent solids basis are preferably present in an amount about 2 wt% to about 15 wt%, and, more preferably, about 5 wt% to about 10 wt%.

Arylsulfonamide epoxy resins may also be included. For example, tosylamide epoxy resin may be added to the composition. Such arylsulfonamide epoxy resins enhance the aesthetics and gloss of the composition, but are not necessary to the functioning of the invention. When used, arylsulfonamide epoxy resins are preferably present in an

amount about 1 wt% to about 15 wt% and, more preferably, about 3 wt% to about 8 wt%.

One or more plasticizers may also preferably be included in cosmetic compositions according to the present invention, but are not essential. When used, the plasticizer preferably is present in an amount about 1 wt% to about 9 wt% and, more preferably, about 2 wt% to about 5 wt%. Plasticizers useful in the present invention are those known in the art, including, without limitation, dibutyl phthalate (DBP) and other phthalates, tributyl acetyl citrate and other citrates, ethyl toluene sulfonamide (ethyl tosylamide), n-cyclohexyl para-toluene sulfonamide, glycerol and other glycols, glycol ethers, glycol esters, hydrogenated castor oil or epoxidized oils, polyesters, polybutylenes, low-MW aliphatic polyurethanes (about 2000 to about 5000 MW), toluene sulfonamide urea formaldehyde, γ -butyral lactone, n-butylphthalimide/isopropylphthalimide, ethylhexyl diphenyl phosphate, wool fat derivatives, chlorinated paraffins, glyceryl triacetate, camphor, sucrose acetate isobutyrate (SAIB), "slow" or high boiling solvents, low t_g resins and polymers, and mixtures thereof. A more preferred cosmetic composition according to the present invention has ethyl toluene sulfonamide in an amount about 0.5 wt% to about 5 wt%.

Conventional nail polish compositions have phthalates, such as DBP, as an essential component for imparting flexibility to the nail polish coating. It is highly surprising and unexpected that the nail polish compositions of the

present invention can possess superior flexibility in the absence of phthalates, such as DBP.

The present invention may also have a solvent in an amount about 45 wt% to about 95 wt% and, more preferably, about 60 wt% to about 80 wt%. Examples of solvents useful in the present invention include, without
5 limitation, alkylacetates, arylacetates, alcohols, ethers, ketones, alkanes, hydrocarbons, and water. Preferably, the cosmetic composition is anhydrous. More preferably, a cosmetic composition according to the present invention has butyl acetate in an amount about 20 wt% to about 40
10 wt%, ethyl acetate in an amount about 20 wt% to about 40 wt%, ethyl alcohol in an amount about 5 wt% to about 10 wt%, isopropanol in an amount about 1 wt% to about 10 wt% (more preferably about 3 wt% to about 6 wt%), and diacetone alcohol in an amount 0.5 wt% to about 5 wt%.

Additional ingredients that may be included in cosmetic
15 compositions according to the present invention include stabilizing agents and pigments. When used, stabilizing agents, such as stearylalkonium bentonite and stearylalkonium hectorite, are present preferably in an amount about 0.1 wt% to about 3 wt% and, more preferably, about 0.75 wt% to about 1.5 wt%. In a most preferred embodiment for a nail polish, the
20 stearylalkonium bentonite and stearylalkonium hecorite are present in about an equal amount. Furthermore, pigments are preferably present in an amount about .01 wt% to about 10 wt% and, more preferably, about 0.5 wt% to about 4 wt%.

Moreover, the present invention may include any other suitable ingredient, limited only by the purpose to which the cosmetic composition is intended. For example, a cosmetic composition according to the present invention may include: ultraviolet light absorbers, antioxidants, fragrances, moisturizers, medicaments, humectants, fillers, or mixtures thereof.

The following is an example of a cosmetic composition according to the present invention.

10

Example 1: Cosmetic Composition

<u>Ingredient</u>	<u>Approximate wt%</u>
solvent	45 - 95
primary film former	5 - 15
high-MW polyurethane resin	2 - 15
plasticizer	1 - 9
stabilizing agent	0.1 - 3
pigment	0.01 - 10

20

The following is an example of a nail polish according to the present invention.

Example 2: Nail Polish

<u>Ingredient</u>	<u>Approximate wt%</u>
butyl acetate	20 - 40
ethyl acetate	20 - 40
ethyl alcohol	5 - 10
isopropanol	1 - 10
diacetone alcohol	0.5 - 5
nitrocellulose	5 - 15
high-MW polyurethane	2 - 15
tosylamide epoxy resin	1 - 15
ethyl tosylamide	0.5 - 5

25

30

stearalkonium hectorite	0.05	-	1.5
stearalkonium bentonite	0.05	-	1.5
pigments	0.01	-	10

5

Example 3

Nail polish composition A was formulated in accordance with Example 2. Nail polish composition B was similarly formulated, except composition B contained no high MW polyurethane. Compositions A and B were each cast onto a substrate, such as glass, dried for twenty four hours at ambient temperature to create a film, cut into sections approximately 1 inch by 4 inches by 0.001 inch thick, peeled from the substrate and placed onto an Instron apparatus to determine their mechanical properties.

Composition A film and composition B film were each stressed or pulled by the Instron at the rate of 6 inches/minute. The displacement (inches) of each film was recorded at film fracture and is set forth below.

	<u>Composition A</u>	<u>Composition B</u>
20 Displacement	4.657 inches	0.064 inches

The present invention having been described with particular reference to the preferred forms thereof, it will be obvious that various changes and modifications may be made herein without departing from the spirit and scope of the invention as defined in the appended claims.

Wherefore We Claim:

1. A cosmetic composition comprising:
a cellulose-based film forming agent; and
5 a polyurethane resin having a molecular weight about 20,000 to about 80,000.
2. The composition of claim 1, wherein said cellulose-based film forming agent is nitrocellulose.
- 10 3. The composition of claim 1, wherein said cellulose-based film forming agent is present in an amount about 5 wt% to about 15 wt% of the total weight of the composition.
- 15 4. The composition of claim 1, wherein said polyurethane resin has a t_g of about -4°C to about -20°C .
5. The composition of claim 1, wherein said polyurethane resin is selected from the group consisting of the general structures:
20 $[-\text{O}-(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_{20}-\text{C}(\text{O})-\text{NH}-\text{R}-\text{NH}-\text{C}(\text{O})-]$;
 $[-\text{O}-(\text{CH}_2-\text{CH}_2\text{CH}_2\text{CH}_2-\text{O})_{10}-\text{C}(\text{O})-\text{NH}-\text{R}-\text{NH}-\text{C}(\text{O})-]$;
and combinations thereof, wherein R is an aliphatic moiety.

6. The composition of claim 1, wherein said polyurethane resin is present in an amount about 2 wt% to about 15 wt% of the total weight of the composition.

5 7. The composition of claim 1, further comprising a arylsulfonamide epoxy resin.

8. The composition of claim 7, wherein said arylsulfonamide epoxy resin is tosylamide epoxy resin.

10

9. The composition of claim 7, wherein said arylsulfonamide epoxy resin present in an amount about 1 wt% to about 15 wt% of the total weight of the composition.

15 10. The composition of claim 1, further comprising a solvent in an amount about 45 wt% to about 95 wt% of the total weight of the composition.

11. The composition of claim 1, further comprising a plasticizer.

20

12. The composition of claim 11, wherein said plasticizer is about 1 wt% to about 9 wt% of the total weight of the composition.

13. The composition of claim 1, further comprising at least one of a stabilizing agent and a pigment.

14. A cosmetic composition comprising:

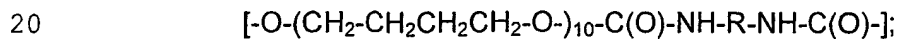
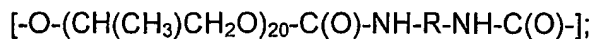
5 a cellulose-based film forming agent present in an amount about 5 wt% to about 15% by weight of the total weight of the composition; and
a polyurethane resin having a molecular weight about 20,000 to about 80,000 and present in an amount about 2 wt% to about 15 wt% by weight of the total weight of the composition.

10

15. The composition of claim 14, wherein said cellulose-based film forming agent is nitrocellulose.

16. The composition of claim 14, wherein said polyurethane resin
15 has a t_g of about -4°C to about -20°C .

17. The composition of claim 14, wherein said polyurethane resin is selected from the group consisting of the general structures:



and combinations thereof, wherein R is a non-aromatic moiety.

18. The composition of claim 14, further comprising an arylsulfonamide epoxy resin in an amount about 1 wt% to about 15 wt% of the total weight of the composition.

5 19. The composition of claim 18, wherein said arylsulfonamide epoxy resin is tosylamide epoxy resin.

20. The composition of claim 18, further comprising a plasticizer present in an amount about 1 wt% to about 9 wt% of the total weight of the
10 composition.

21. A cosmetic composition comprising:
a solvent in an amount about 45 wt% to about 95 wt%;
a primary film former in an amount about 5 wt% to about 15 wt%;
15 a high molecular weight polyurethane resin in an amount about 2 wt% to about 15 wt%;
a plasticizer in an amount about 1 wt% to about 9 wt%;
a stabilizing agent in an amount about 0.1 wt% to about 3 wt%; and
a pigment in an amount about 0.01 wt% to about 10 wt% of the total
20 weight of the composition.

22. A cosmetic composition comprising
about 20 wt% to about 40 wt% butyl acetate;

about 20 wt% to about 40 wt% ethyl acetate;

about 5 wt% to about 15 wt% nitrocellulose;

about 2 wt% to about 15 wt% high molecular weight polyurethane;

and

5 about 1 wt% to about 15 wt% tosylamide epoxy resin.

23. The composition of claim 22, further comprising about 0.01 wt% to about 10 wt% pigment.

10 24. A method of imparting an improved flexible, durable and/or transfer resistant cosmetic coating to human nails comprising applying to the nails the composition of claim 1.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/43485

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : A61K 7/025

US CL : 424/64

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 424/64

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,093,108 A (PAPPAS et al) 03 March 1992, column 9, lines 13-68, column 10, columns 11,13 and 14.	1-24
Y	US 6,080,413 A (ELLINGSON et al) 27 June 2000, column 3, lines 40-67, column 4, lines 1-16, column 5, lines 45-50 and column 8, lines 4-12.	1-24

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T"

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X"

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y"

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"

document member of the same patent family

Date of the actual completion of the international search

27 March 2002 (27.03.2002)

Name and mailing address of the ISA/US

Commissioner of Patents and Trademarks

Box PCT

Washington, D.C. 20231

Facsimile No. (703)305-3230

Date of mailing of the international search report

18 APR 2002

Authorized officer

Sharon L. Howard

Telephone No. (703) 308-1234